



⑪ Publication number : **0 530 974 A1**

⑫ **EUROPEAN PATENT APPLICATION**

⑳ Application number : **92307053.6**

⑤① Int. Cl.<sup>5</sup> : **A61K 7/06**

㉔ Date of filing : **03.08.92**

③① Priority : **05.08.91 GB 9116871**

④③ Date of publication of application :  
**10.03.93 Bulletin 93/10**

⑧④ Designated Contracting States :  
**AT BE CH DE DK ES FR GB GR IE IT LI NL PT SE**

⑦① Applicant : **UNILEVER PLC**  
**Unilever House Blackfriars**  
**London EC4P 4BQ (GB)**

⑧④ **GB IE**

⑦① Applicant : **UNILEVER N.V.**  
**Weena 455**  
**NL-3013 AL Rotterdam (NL)**

⑧④ **BE CH DE DK ES FR GR IT LI NL PT SE AT**

⑦② Inventor : **Birtwistle, David Howard**  
**18 Exmoor Close**  
**Irby, Wirral L61 9QN (GB)**

⑦④ Representative : **Ford, Michael Frederick et al**  
**MEWBURN ELLIS 2 Cursitor Street**  
**London EC4A 1BQ (GB)**

⑤④ **Hair care composition.**

- ⑤⑦ A hair care composition suitable for use as a shampoo comprises ;
- (a) at least one surfactant ;
  - (b) at least one water-insoluble end-functionalised quaternary silicone polymer capable of dissolving in said at least one surfactant ; and
  - (c) a cationic deposition polymer.

**EP 0 530 974 A1**

The present invention relates to hair care compositions and in particular to clear or opaque hair care compositions containing quaternary silicones.

Conventional silicone-containing hair care compositions, e.g. conditioning shampoos, frequently give rise to static build-up on hair which results in the problem known as 'fly-away'; that is, hair which looks fluffy and resists combing control.

Typically, such silicone-containing hair care compositions of the prior art are opaque systems and it is known that such silicone-containing opaque systems give rise to flyaway or loss of combing control of hair.

GB-A-2161172 for example describes a shampoo system comprising a quaternised polymer and organo-functional silicone. However the silicones disclosed for use in that system are water-soluble "comb" polymers and give rise to hair care compositions which are opaque or cloudy in appearance. A "comb" polymer, for the purposes of the description, is a long chain silicone polymer wherein functional groups are found scattered at various points, often randomly, along the length of the chain. Furthermore, such water-soluble silicone comb polymers have limited conditioning and non-flyaway efficacy, since their water-solubility leads to poor deposition from aqueous based shampoo compositions.

Similar disadvantages are encountered with other water-soluble silicone comb polymers also known in the art, for example the quaternary silicone polymers that are disclosed in GB-A-2157168 and GB-A-2144329.

What has now been surprisingly found is that by utilising certain water-insoluble quaternary silicones capable of dissolving in surfactant, particularly anionic surfactant, the problems associated with the prior art may be reduced. In particular, by utilising water-insoluble quaternary silicones which are not comb polymers as defined above, improved conditioning and non-flyaway benefits may be obtained over the prior art and it is possible to prepare particularly effective hair conditioning shampoo compositions which are optically clear.

According to the present invention there is provided a hair care composition suitable for use as a shampoo, comprising:

(a) at least one surfactant;

(b) at least one water-insoluble end-functionalised quaternary silicone polymer capable of dissolving in said at least one surfactant; and

(c) a cationic deposition polymer.

The invention will now be described in detail.

### (a) Surfactant

The hair care composition of the invention comprises at least one surfactant which may be selected from anionic, nonionic, amphoteric and zwitterionic surfactants or mixtures thereof.

Suitable anionic surfactants include the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkyl succinates, alkyl sulphosuccinates, N-alkyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, and alpha-olefin sulphonates, especially their sodium, magnesium, ammonium and mono-, di- and triethanolamine salts. The alkyl groups generally contain from 8 to 18 carbon atoms and may be unsaturated. The alkyl ether sulphates, alkyl ether phosphates and alkyl ether carboxylates may contain from 1 to 10 ethylene oxide or propylene oxide units per molecule, and preferably contain 2 to 3 ethylene oxide units per molecule.

Examples of suitable anionic surfactants include sodium oleyl succinate, ammonium lauryl sulphosuccinate, ammonium lauryl sulphate, sodium dodecylbenzene sulphonate, triethanolamine dodecylbenzene sulphonate and sodium N-lauryl sarcosinate. The most preferred anionic surfactants are sodium lauryl sulphate, triethanolamine lauryl sulphate, triethanolamine monolauryl phosphate, sodium lauryl ether sulphate 1EO, 2EO and 3EO, ammonium lauryl sulphate and ammonium lauryl ether sulphate 1EO, 2EO and 3EO.

The nonionic surfactants suitable for use in the composition of the invention may include condensation products of aliphatic ( $C_8 - C_{18}$ ) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having from 6 to 30 ethylene oxide groups.

Other suitable nonionics include mono- or di-alkyl alkanolamides. Examples include coco mono- or di-ethanolamide and coco mono-isopropanolamide.

The amphoteric surfactants suitable for use in the composition of the invention may include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines, alkyl glycinates, alkyl carboxglycinates, alkyl amphopropionates, alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates wherein alkyl and acyl groups have from 8 to 18 carbon atoms. Examples include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl betaine and sodium cocamphopropionate.

The at least one surfactant or mixture of surfactants may be present in the hair care composition of the invention in a total amount of from about 5 to about 40% by weight, more preferably from about 5 to about 20% by weight.



parency, medium viscosity guar derivative having a low degree of substitution.

Suitable cationic cellulose derivatives as deposition polymers include the Polymer JR series, ex Union Carbide.

5 The compositions of the invention may contain from about 0.01 to 1% by weight of the cationic deposition polymer, preferably from about 0.04 to about 0.5% by weight.

#### Other Components

10 The compositions of the present invention may also contain as optional components cosurfactants which act as foam modifying components. Such foam modifying components may be present in amounts up to about 10% by weight, preferably in amounts of from about 1.5% to about 3% by weight. Suitable cosurfactants include betaines such as cocoamidopropyl betaine, lauryl dimethyl betaine, cocodimethyl sulphopropyl betaine and the like. Other suitable cosurfactants include such surfactants as mono- or dialkyl alkanolamides (e.g. coco-diethanolamide), amine oxides (eg lauryl amine oxide), glycinate, propionates, sultaines and the like.

15 The hair care compositions of the invention will frequently, and advantageously, be optically clear or translucent. However, opaque or cloudy formulations in accordance with the above defined composition are still within the scope of the invention.

If desired, the compositions of the invention may also contain a suitable amount of one or more opacifiers, e.g. ethylene glycol distearate, PEG-3 distearate.

20 The shampoo compositions of the present invention may contain other components in minor amounts commonly found in shampoo compositions, such as antibacterial agents, antidandruff agents such as zinc pyridinethione or Octopirox, pearlescers, perfumes, dyes, colouring agents, preservatives, viscosity modifiers, proteins, polymers, buffering agents, polyols and other moisturising agents, plant extracts such as seaweed extracts, herb extracts and the like.

25 In a further aspect of the present invention there is provided a method of preparing the hair care composition defined above. In the method, surfactant(s) and water are mixed together, reaching homogeneity. Cationic polymer, e.g. guar hydroxypropyl trimonium chloride, may be added either as a solid or as a solution in water. The resulting mixture may then be stirred until homogeneous. Quaternary silicone may then be added and mixed in under high shear mixing if appropriate, until the mixture is substantially homogeneous. Remaining components, such as sodium chloride, perfume, colouring and like, may then be added under typical mixing conditions.

30 In yet a further aspect of the present invention, use of the hair care composition entails wetting the hair, then adding shampoo to the hair, typically of the order of about 5 to 10 grams of shampoo, and massaging the hair to generate a rich lather. The hair may then be rinsed until the foam is washed out. The process may be repeated.

35 The invention will now be illustrated by the following examples. It is to be understood that the examples are not to be viewed as limiting in any way the scope of the appended claims. All amounts are expressed in % by weight, unless otherwise stated.

#### 40 Examples 1 to 21

The following hair conditioning shampoo compositions were prepared according to the method described above. The compositions of Examples 1 to 14 were optically clear, whereas those of Examples 15 to 20 were opaque.

Example	1	2	3	4	5	6	7	8	9	10
SLES 2EO	16	16	16	16	16	16	-	-	-	-
Ammonium lauryl sulphate	-	-	-	-	-	-	12	12	12	12
SLES 3EO	-	-	-	-	-	-	-	-	-	-
Cocoamidopropyl betaine	2	2	2	2	2	2	-	-	-	-
Lauryl dimethyl betaine	-	-	-	-	-	-	2	2	2	2
Quaternary silicone*	0.1	0.25	0.5	0.1	0.25	0.5	0.4	0.4	0.4	0.4
Jaguar C13S	0.1	0.1	0.1	0.04	0.04	0.04	-	-	-	-
Jaguar C17	-	-	-	-	-	-	0.05	0.1	0.3	0.5
Jaguar C162	-	-	-	-	-	-	-	-	-	-
Jaguar C16	-	-	-	-	-	-	-	-	-	-
Ethylene glycol distearate	-	-	-	-	-	-	-	-	-	-
PEG-3 distearate	-	-	-	-	-	-	-	-	-	-
Perfume, dyes etc	q.v.	q.v.	q.v.	q.v.	q.v.	q.v.	q.v.	q.v.	q.v.	q.v.
Sodium chloride	1	1	1	1	1	1	-	-	-	-
Ammonium chloride	-	-	-	-	-	-	1.5	1.5	1.5	1.5
Water	to 100	to 100	to 100	to 100	to 100	to 100	to 100	to 100	to 100	to 100

\* K3474 (ex Goldschmidt)

Example	11	12	13	14	15	16	17	18	19	20
SLES 2EO	-	-	-	-	16	16	14	12	16	13
Ammonium lauryl sulphate	-	-	-	-	-	-	-	-	-	-
SLES 3EO	14	14	14	14	-	-	-	-	-	-
Cocoamidopropyl betaine	-	-	-	-	2	2	4	2	2	4
Lauryl dimethyl betaine	3	3	3	3	-	-	-	-	-	-
Quaternary silicone*	0.2	0.2	0.2	0.2	0.2	0.5	0.1	0.2	0.5	0.1
Jaguar C13S	0.1	-	-	-	0.1	0.1	0.1	0.1	0.1	0.1
Jaguar C17	-	0.06	-	-	-	-	-	-	-	-
Jaguar C162	-	-	0.5	-	-	-	-	-	-	-
Jaguar C16	-	-	-	0.3	-	-	-	-	-	-
Ethylene glycol distearate	-	-	-	-	0.5	0.7	1.0	-	-	-
PEG-3 distearate	-	-	-	-	-	-	-	1.0	0.7	0.5
Perfume, dyes etc	q.v.	q.v.	q.v.	q.v.	q.v.	q.v.	q.v.	q.v.	q.v.	q.v.
Sodium chloride	1.5	1.5	1.5	1.5	1.0	1.0	1.0	1.5	1.0	1.0
Ammonium chloride	-	-	-	-	-	-	-	-	-	-
Water	to 100	to 100	to 100	to 100	to 100	to 100	to 100	to 100	to 100	to 100

\* K3474 (ex Goldschmidt)

Comparative Example 1

The following shampoo compositions A and B were prepared as described above. Composition A (which was optically clear) was in accordance with the invention, while Composition B included instead a water-soluble quaternary silicone polymer (ABIL-QUAT 3272, ex Goldschmidt) of a corresponding structure to silicone K3474 but in which the value of n in the formula is about 30.

		Composition (%wt)	
		<u>A</u>	<u>B</u>
10	<u>Ingredient</u>		
	SLES 2EO	16	16
	Cocoamidopropyl betaine	2	2
	Silicone K3474	0.5	-
15	Silicone ABIL-QUAT 3272	-	0.5
	Jaguar C13S	0.1	0.1
	Formalin	0.1	0.1
20	Sodium chloride	1.0	1.0
	Water	to 100	to 100

Shampoos A and B were subjected to a paired comparison test for the descriptors ease of dry combing, softness and non-flyaway, using as a control a con-conditioning shampoo formulation corresponding to A or B but excluding silicone.

The voting split for each of the test formulations (vs control) was as follows:

<u>Voting split (maximum 72)</u>		
	<u>A</u>	<u>B</u>
30		
Ease of dry combing	70*	43
Softness	66*	28
35		
Non-flyaway	70*	55
* >99.99% significance.		

Comparative Example 2

The following shampoo composition C was prepared as before:

		<u>C (%wt)</u>
45	<u>Ingredient</u>	
	SLES 3EO	8
	Cocoamidopropyl betaine	4
	Silicone K3474	0.2
	Polymer JR400	0.3
50	Formalin	0.1
	Sodium chloride	2
	Water	to 100

Shampoo C, which was transparent, was subjected to a paired comparison test for the same descriptors and versus the same control as in Comparative Example 1. The voting split (vs control) was as follows:

Voting split (maximum 72)

	<u>C</u>
5	Ease of dry combing 72*
	Softness 66*
	Non-flyaway 72*

\* &gt;99.99% significance.

10

Comparative Example 3

15 The following shampoo composition D in accordance with the prior art was prepared as before. The silicone used was ABIL B9950, as disclosed in GB-A-2161172, which is a water-soluble comb polymer as known from the prior art.

	<u>Ingredient</u>	<u>D (%wt)</u>
	SLES 2EO	16
20	Cocoamidopropyl betaine	2
	ABIL B9950	1
	Jaguar C13S	0.1
25	Formalin	0.1
	Sodium chloride	1.5
	Water	to 100

30 Shampoo D, which was transparent, was subjected to a paired comparison test for the same descriptors and versus the same control as in Comparative Example 1. The voting split (vs control) was as follows:

Voting split (maximum 72)

35

	Ease of dry combing	28
	Softness	33
40	Non-flyaway	36

Each of the above results is statistically non-significant, and in all but the non-flyaway case in favour of the control.

45

Comparative Example 4

50 The following three shampoo compositions E, F and G were prepared as before. Composition E was in accordance with the present invention, while compositions F and G included instead water-soluble quaternary silicone polymers (ABIL B9950 and ABIL B9905, respectively) as disclosed in GB-A-2161172.

55

55



		Composition (%wt)		
		<u>E</u>	<u>F</u>	<u>G</u>
5	<u>Ingredient</u>			
	SLES 2EO	16.24	16.24	16.24
	Coconut diethanolamide	4.00	4.00	4.00
	ABIL B9950*	-	1.00	-
10	ABIL B9905*	-	-	1.00
	K3474*	0.30	-	-
	Jaguar C13S	0.50	0.50	0.50
	Formalin	0.10	0.10	0.10
15	Water	to 100	to 100	to 100

\* amounts quoted compare equivalent actual levels of  
 20 silicone - ABIL B9950 and ABIL B9905 are supplied as 30%  
 active, whereas K3474 is supplied as 100% active.

Compositions E and F were subjected to a paired comparison test between themselves for the descriptors  
 25 dry combability, softness and non-flyaway. The voting split was as follows:

		<u>Voting split (maximum 72)</u>		
		<u>E</u>	vs	<u>F</u>
30	Dry combability	55		17
	Softness	43		29
	Non-flyaway	49		23

35 Compositions E and G were subjected to a similar but half-size paired comparison test, between them-  
 selves, the results of which were as follows:

		<u>Voting split (maximum 36)</u>		
		<u>E</u>	vs	<u>G</u>
40	Dry combability	36		0
	Softness	-*		-*
45	Non-flyaway	36		0

50 \*since ABIL B9905  
 is believed to be  
 toxic, the test for  
 softness was not  
 carried out.

## 55 Claims

1. A hair care composition suitable for use as a shampoo, comprising:

- 5**

- 10

- 15

- 20

- 25



15

- 0

- 5

- 9

- ;

- 3

15. A composition according to any preceding claim, wherein the quaternary silicone polymer is present in the composition in an amount of from 0.01 to 1.0% by weight.
- 5 16. A composition according to any preceding claim, wherein the cationic deposition polymer is a cationic derivative of guar gum or a cationic cellulose derivative.
17. A composition according to any preceding claim, wherein the cationic deposition polymer is present in the composition in an amount of from 0.01 to 1% by weight.
- 10 18. A composition according to any preceding claim, further comprising up to 10% by weight of a cosurfactant selected from betaines, mono- or dialkyl alkanolamides, amine oxides, amine glycinate, amine propionate and amine sultaine.
19. A method of washing hair comprising applying thereto a composition according to any preceding claim.

15

20

25

30

35

40

45

50

55



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 92 30 7053

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	DE-A-3 719 086 (TH. GOLDSCHMIDT AG) 27 October 1988 * whole document, especially example 4 page 11 *	1-19	A61K7/06
Y,D	GB-A-2 161 172 (BEECHAM GROUP PLC) 8 January 1986 * the whole document *	1-19	
Y	EP-A-0 432 951 (UNILEVER PLC) 19 June 1991 * the whole document *	1-19	
Y	EP-A-0 017 121 (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN) 15 October 1980 * the whole document *	1-19	
A	EP-A-0 400 976 (UNILEVER PLC) 5 December 1990 * the whole document *	1-19	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			A61K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 DECEMBER 1992	Examiner GAC G.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  F : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons</p> <p>A : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (12.82 (P0441))